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Thorium speciation in seawater

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Abstract

Since the 1960s, thorium isotopes occupy a special place in the oceanographer's toolbox as tracers for determining rates and mechanisms of oceanic scavenging, particle dynamics, and carbon fluxes. Due to their unique and constant production rates from soluble parent nuclides of uranium and radium, their disequilibrium can be used to calculate rates and time scales of sinking particles. In addition, by ratio-ing particulate ^{234}Th (as well, in principle, other Th-nuclides) to carbon (and other elements), and linking this ratio to the parent–daughter disequilibrium in the water column, it is possible to calculate fluxes of carbon and other elements. Most of these applications are possible with little knowledge of the dissolved chemical properties of thorium, other than its oxidation state (IV) and tendency to strongly sorb to surfaces, i.e., its "particle- or surface-activity". However, the use of any tracer is hindered by a lack of knowledge of its chemical properties. Recent observations in the variability of carbon to ^{234}Th ratios in different particle types, as well as of associations of Th(IV) with various marine organic biomolecules has led to the need for a review of current knowledge and what future endeavors should be taken to understand the marine chemistry of thorium.

Keywords: Thorium; Speciation; Seawater; Colloids; Exopolymeric substances; Transparent exopolymeric particles; Amphiphiles; Biosurfactant ligand

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1. Introduction

The element thorium (Th) is composed of 25 radioisotopes, ranging in atomic mass from 212 to 236, with half-lives of seconds to 10^{10} years (Table 1). Natural Th consists almost entirely of primordial ^{232}Th ($t_{1/2} = 1.4 \times 10^{10}$ years), due to its extremely long half-life relative to the other Th isotopes. As such, when chemical equilibrium is established, ^{232}Th determines the chemical fate and speciation of all Th isotopes. In seawater, ^{232}Th is present at pM concentrations. A number of other Th isotopes (e.g., ^{234}Th, ^{230}Th, ^{228}Th) also exist in seawater, albeit at lower concentrations, e.g., ^{234}Th is present in the ocean at atto-molar (10^{-18} M) concentration levels. These Th isotopes are primarily produced by natural uranium isotopes (^{238}U, ^{235}U and ^{234}U) that are soluble in seawater. In marine systems, Th has proven to be a very useful tracer of a wide range of oceanographic processes ranging from particle cycling (Bacon and Rutgers van der Loeff, 1989; Clegg and Whitfield, 1990, 1991; Dunne et al., 1997) and carbon export flux (e.g., Murray et al., 1989; Buesseler, 1998, and references therein; Benitez-Nelson et al., 2001) to boundary scavenging (Moore, 1981; Anderson et al., 1994; Santschi et al., 1999, Smoak et al., 2000) and paleocirculation (Yu et al., 1996; Marchal et al., 2000; Moran et al., 2002). This is because Th's chemical properties are relatively simple: Th has only one stable oxidation state, IV, under all redox conditions in natural waters, and Th (IV) ions are extremely particle reactive.

Over the past several decades, one isotope of Th, ^{234}Th ($t_{1/2} = 24.1$ days), has been increasingly used as a tracer of short-term particle and carbon removal from the upper ocean via sinking particles. Organic carbon export or "export production" is often assumed, at steady state, to be equal to the flux of new nutrients into the euphotic zone. In essence, once ^{234}Th is produced (via decay of ^{238}U) in seawater, it is rapidly "scavenged" by the surrounding particle regime within days to few months. In its most basic sense, the difference between the ^{234}Th produced from ^{238}U and what is actually measured in the water, can be assumed to be due to removal by sinking particles (Savoye et al., 2006-this issue). This ^{234}Th flux is then used with a site and time specific carbon (C)/^{234}Th ratio to convert ^{234}Th fluxes into those of C. Other elemental and compound fluxes can be calculated using the same approach (e.g., Bacon et al., 1996; Gustafsson et al., 1997a,b; Rutgers van der Loeff et al., 2002; Weinstein and Moran, 2005). Measured C/^{234}Th ratios vary significantly with region, season, depth and sample type, and reasons for this variability remain poorly understood (see Buesseler et al., 2006-this issue). Thus, as the use of ^{234}Th as an export tracer becomes more wide spread, it is essential that we understand the mechanisms that control its particle reactivity beyond the typical "blackbox" approach. At the very least, an improved knowledge of the chemical speciation of Th would allow one to better resolve and assess the variability of C/^{234}Th ratios, as well as its use as a probe of other biogeochemical processes in the ocean.

2. Inorganic Th speciation

The prevailing inorganic species of Th in seawater at pH of 8 are hydroxo (Choppin and Wong, 1998) and carbonato complexes, in approximately equal proportions (Bruno, 1990; Östhols et al., 1994; Murphy et al., 1999). In fact, in organic-free solutions, thorium, an A-type metal ion, will strongly hydrolyze to form polyhydroxy colloidal complexes. Other strong ligands include carbonate, humics, phosphate, ethylene-diamine-tetraacetic acid (EDTA) and diethyl-triamine-pentaacetic acid (DTPA) (Tables 2a and 2b). The solubility of Th

Table 1
Radioisotopes of thorium (NAS-NS-3004, 1960; http://www.hps.org/publicinformation/radardecaydata.cfm?Element=Th)

Isotope	Half-life	Type of decay	Main decay energy (MeV)	Method of production
^{234}Th	24.1 days	β^-	0.053 (70%)	Natural radioactivity; daughter of ^{238}U
^{233}Th	22.1 min	β^-	1.245 (87%)	^{232}Th+neutrons
^{232}Th	1.39×10^{10} years	α	4.012 (78%)	Natural thorium is 100% ^{232}Th
^{231}Th	25.64 h	β^-	0.080 (37%)	Natural radioactivity; daughter of ^{235}U
^{230}Th	7.5×10^4 years	α	4.687 (76%)	Natural radioactivity; daughter of ^{234}U
^{229}Th	7340 years	α	4.845 (56%)	Daughter of ^{233}U
^{228}Th	1.9 years	α	5.423 (72%)	Natural radioactivity; daughter of ^{228}Ac
^{227}Th	18.17 days	α	6.038 (24%)	Natural radioactivity; daughter of ^{227}Ac
^{226}Th	30.9 min	α	6.337 (76%)	Daughter of ^{230}U
^{225}Th	8 min	α	6.48 (43%)	Daughter of ^{229}U
^{224}Th	~1 s	α	7.17 (81%)	Daughter of ^{228}U
^{223}Th	~0.7 s	α	7.29 (60%)	Daughter of ^{227}U